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Electron microscopy of banded structures in oriented thermotropic polymers

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Banded microstructures in thermotropic polymers are analysed by transmission electron microscopy. The banded structures are only apparent in dark field and lie normal to the direction of the shear imposed on the sample when above its softening temperature. Dark field micrographs prepared from different regions of the diffraction pattern demonstrate that the structures are associated with the serpentine path of the polymer molecules about the shear direction.

1. Introduction

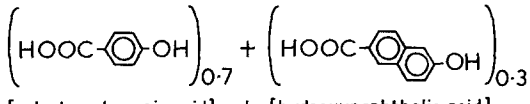
In the preceding paper [1], the results of an optical microscopy study of banded structures, formed in oriented thin films of several thermotropic liquid crystalline polymers, have been presented. The analysis shows that the orientation of the optical director varies in a systematic manner about the extension axis, and can be approximated by a sine curve. If the director is equivalent to the molecular backbone, this organisation is reminiscent of the "pleated sheet" structure proposed by Dobb *et al.* [2] for the lyotropic polymer, poly(p-phenylene terephthalamide), produced commercially as Kevlar fibre.

In the "pleated sheet" model, the molecular packing follows a zig-zag rather than sinusoidal trajectory, with the angle between successive pleats being about 170°. The transition from one orientation to the other is relatively abrupt. The "pleated sheet" model for Kevlar was originally based on a transmission electron microscopy (TEM) study of ultramicrotomed longitudinal sections of the fibre, but it was subsequently shown [3] that it was also manifest in the polarizing microscope, where alternate regions of transmission and extinction are seen between crossed polars when one of the polars is aligned with the shear axis. This structure, since termed the "banded structure" [1, 4] has now been shown (by light microscopy) to be present in a wide range of polymers exhibiting liquid crystalline order.

The aim of this paper is to examine by electron microscopy specimens which show banded microstructures when viewed with the polarizing microscope, with the specific objective of determining whether the serpentine path of the optical director can be directly related to the molecular trajectory. Such an analysis also permits a direct comparison to be made with the supramolecular packing found in Kevlar.

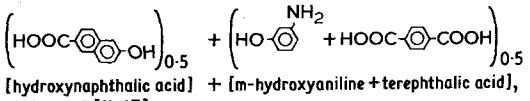
2. Experimental details

Of the four thermotropic polymers discussed in [1], that based on p-hydroxybenzoic acid and hydroxynaphthalic acid residues proved most amenable for study in the TEM, because its relative resistance to the electron beam permitted at least two dark field images of the same region to be photographed before significant beam damage had occurred. This polymer is a random copolyester whose structure may be considered to consist of the following components:



[p-hydroxybenzoic acid] + [hydroxynaphthalic acid]

and is designated (B–N). A few experiments were also carried out on a second polymer based on hydroxynaphthalic acid and m-hydroxyaniline reacted with terephthalic acid. These residues are represented by



[hydroxynaphthalic acid] + [m-hydroxyaniline + terephthalic acid], designated [N-AT].

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The specimen preparation for both polymers was the same: thin oriented films were prepared on a rocksalt substrate by shearing the polymer onto the crystal with a glass slide at a temperature of 300° C, about 20° above the onset of flow, after which it was quenched on a metal block. The film was then carbon coated, the rocksalt dissolved, and the film well washed in a water bath from which it was picked up on a copper grid. Optical examination of films produced in this way confirmed the presence of a banded structure which was the same as that seen in the films produced on a glass substrate, and described in detail in [1]. The specimens were examined in a Philips 300 electron microscope operating at 100 keV. Pairs of dark field images were obtained by using two independent dark field channels between which rapid switching was possible. Each channel permitted the desired part of the diffraction pattern to be brought onto the optic axis of the microscope.

3. Results

A selected area electron diffraction pattern for (B–N) taken from about 2.5 μm is shown in Fig. 1, together with a bright field electron micrograph from the same area. The diffraction pattern shows several features of interest. Pronounced, but far from perfect, orientation is demonstrated by the signficant arcing of both the principal meridional and equatorial reflections. The meridional reflection is sharp, whereas the width of the equatorial reflection indicates a range of lateral periodicities. A sharp inner component to the equatorial reflection is also present, such as may be found in semicrystalline polymers [5]. This sharp component rapidly fades upon irradiation. Other weaker meridional and off-meridional reflections also occur, but these will not be considered further here. There is no evidence to indicate full three dimensional crystallinity as occurs in Kevlar. From the bright field image shown in Fig. 1b, it can be seen that the method of specimen preparation causes substantial variations in the film thickness, with regions of constant thickness elongated along the direction of shear. This uneven contrast is in fact advantageous for these particular experiments since they enable ready correlation between the diffraction pattern and the shear axis (as in Figs. 1a and b), and confirm that the average molecular orientation lies along the direction of shear. Furthermore they also permit immediate identification of the shear direction in dark field images alone.

Due to the angular spread of the arced equatorial reflection, it is possible to form dark field images from different portions of it by the use of a small (50 μm) objective aperture. Fig. 2a shows schematically the position for the objective aperture for the two dark field images presented in Figs. 2b and c. These two positions will be termed the two "wings" of the equatorial. Clearly a continuous range of positions for the objective aperture is possible, tranversing from one "wing" through the centre to the other "wing"; in practice such a range of dark field images is impossible to

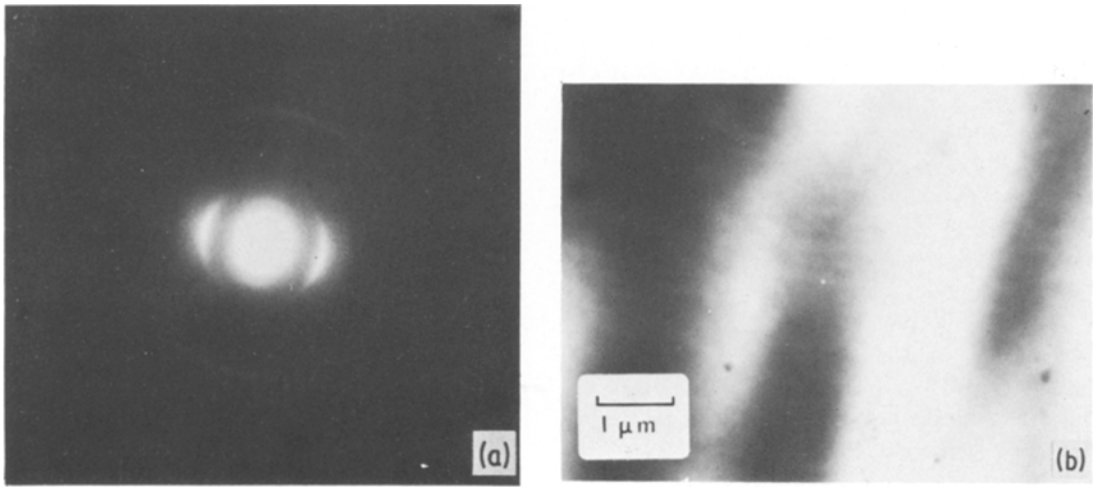

Figure 1 (a) Selected area electron diffraction pattern for B–N, taken from about 2.5 μm. (b) Bright field micrograph of the area from which Fig. 1a was obtained.

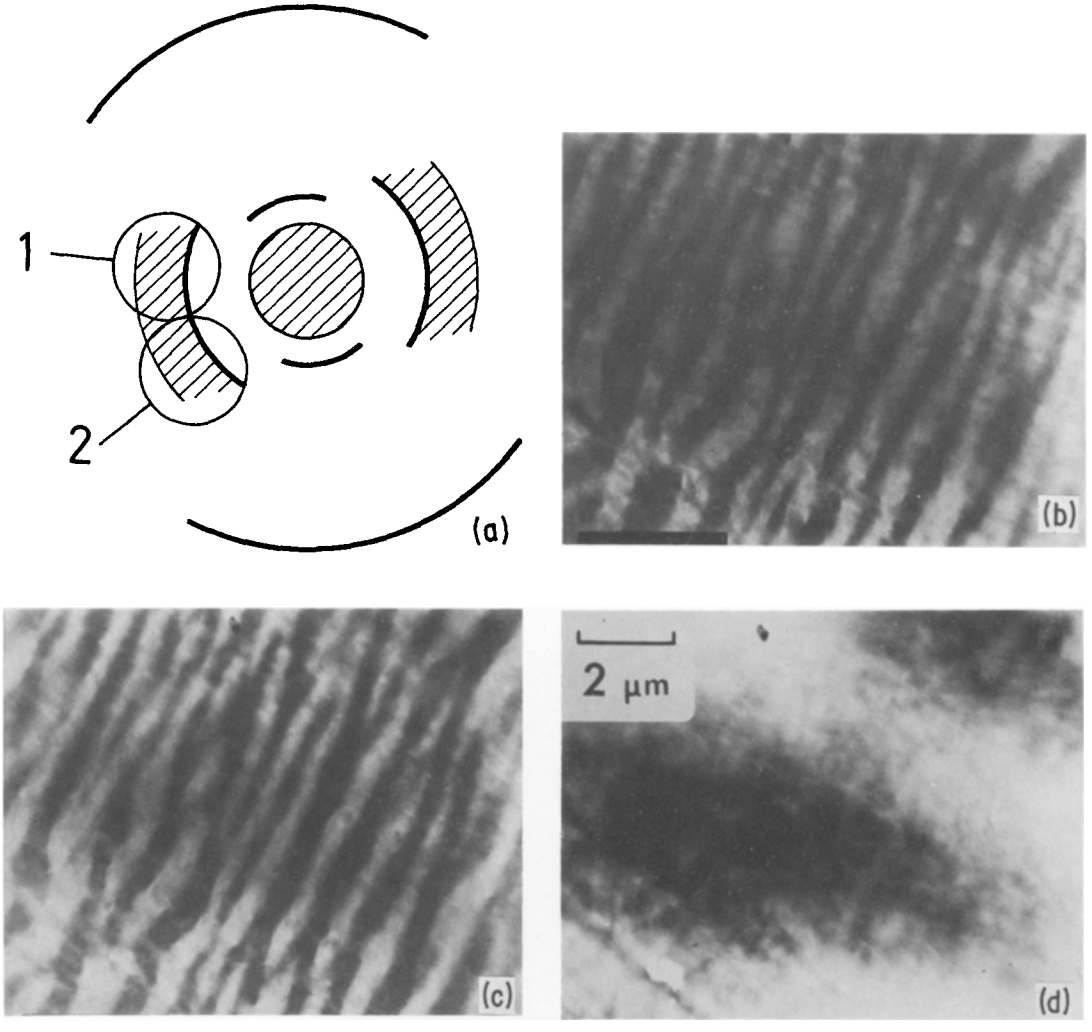

Figure 2 (a) Schematic drawing of the diffraction pattern of B–N, indicating the position of the objective aperture for dark field imaging in the two "wings" of the equatorial reflection. (b) and (c) Dark field images of B–N taken in the two "wings" of the equatorial reflection. (d) Corresponding bright field image.

achieve, due to the beam sensitivity of the material, and only pairwise correlation of dark field images can be performed.

Figs. 2b and c slow bands of alternating diffracting and non-diffracting regions. Changes in the overall contrast level are attributable to the thickness variations discussed above, and these are more clearly visible in the bright field image of Fig. 2d. From these thickness variations it is clear that the diffracting bands lie normal to the shear direction; the average spacing between successive bright bands is about 0.8 μm, which is similar to but slightly less than that observed optically for the periodicity of the banded structure [1, 4]. Comparison of the two dark field images shows that, for these two positions of the objective aperture where the image is formed first in one half of the equatorial and then the other, the images are complementary: a band which is non-diffracting for one objective aperture position, is diffracting for the other, and conversely. This observation demonstrates that the bands comprise regions of systematically varying orientations. The absence of any banding normal to the shear direction in the bright field image precludes these effects being simply connected with variations in the specimen thickness.

Figs. 3a and b show the effect of moving the objective aperture from near the centre of the equatorial to a position on the adjacent wing of the reflection. In this case the width of the diffracting region increases as the aperture is

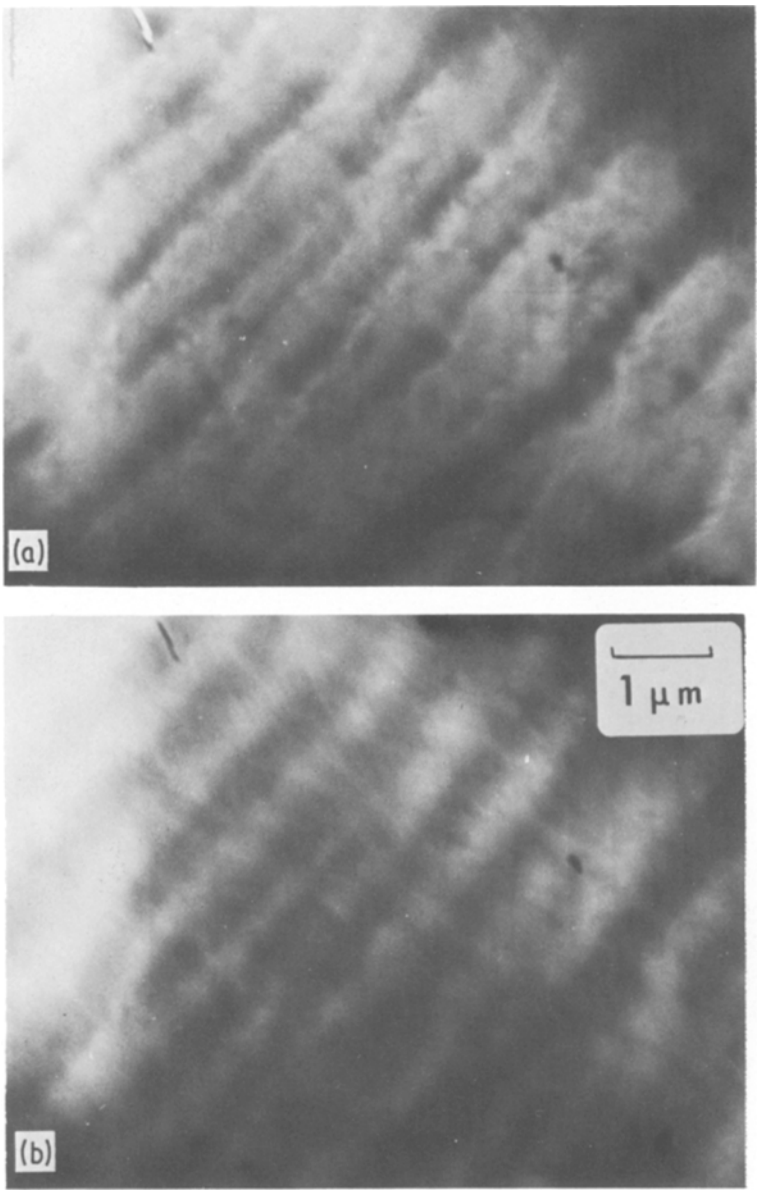

Figure 3 (a) Dark field image formed with the objective aperture near the centre of the equatorial reflection. (b) Corresponding dark field image formed in the wing of the equatorial reflection (on the same side of the centre as Fig. 3a).

moved towards the centre, and the contrast is in the same sense rather than complementary.

Figs. 4a and b are two dark field images formed from one wing and the exact centre of the equatorial reflection. Comparison of these two micrographs shows that the apparent periodicity is halved for the dark field image formed from the central portion of the equatorial, relative to one wing. Imaging in the two wings of the meridional also leads to a banded structure (Figs. 5a and b), but when the dark field image is formed from the central region of the meridional, the overall contrast is nearly uniform with only faint indications of the banded structure (Fig. 6).

Throughout the specimens, the banding is far from regular. New bands tend to start (or stop) at points of sudden thickness variation. Very near the edge of a film, the period tends to decrease substantially, as can be seen in Fig. 7, but less drastic period changes also occur frequently and apparently randomly throughout the specimen.

Although a detailed study has only been carried out on B–N, a few experiments have also been performed on N–AT. Fig. 8 shows a typical

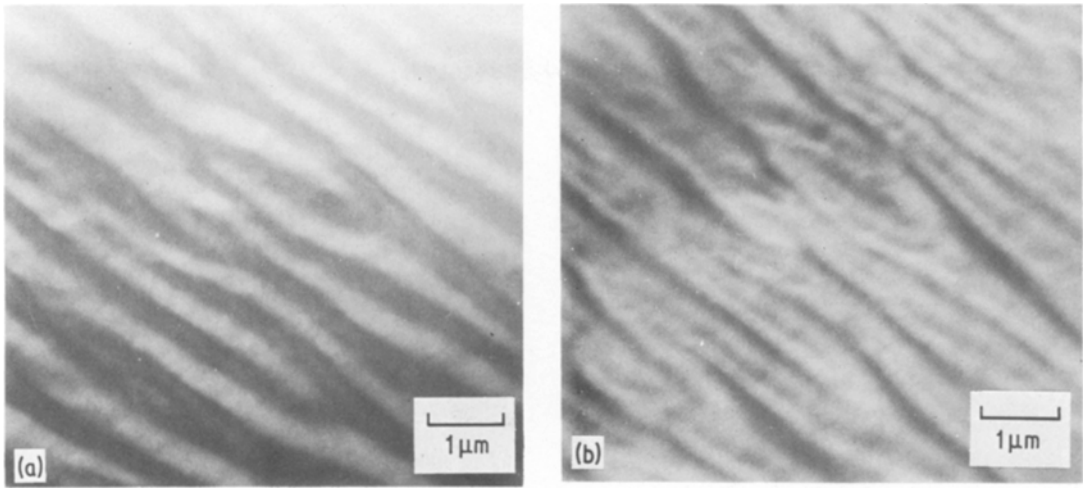

Figure 4 (a) Dark field image formed in one wing of the equatorial reflection. (b) Corresponding dark field image formed from the centre of the equatorial reflection.

dark field image for N–AT formed in one wing of the equatorial arc of the diffraction pattern; it is clear that the same banded structure is present in N–AT as was seen in B–N.

4. Discussion

In the preceding paper [1] it was demonstrated that the banded microstructures of sheared thermotropic films were caused by the serpentine path of the extinction directions about the shear axis. Although it was tempting to equate the optical director with the long axis of the molecules (or the normal to this axis), it was noted that there is no real justification for this. In fact, the confusion which arises in the small molecule liquid crystal field from too casual an association of molecular and optical directors has already been discussed by Frank [6].

The dark field electron micrographs, while generally corroborating the optical evidence for banded microstructures, provide at the same time important additional information. By appropriate positioning of the objective aperture, over a selected part of the diffraction pattern, only those areas with correct molecular alignment will contribute to the dark field image. In this way the banded microstructure and the molecular director can be directly correlated. Analysis of an electron diffraction pattern from a suitably small region would lead to a precise determination for the local molecular director, which for polymers can be taken as the long axis of the molecule. However, because the diffraction patterns are taken from a region about 2.5 μm in diameter, which therefore incorporates several periods of the banded structure, they cannot be used to measure the local orientation and the dark field micrograph shows those areas which correspond to a particular, but

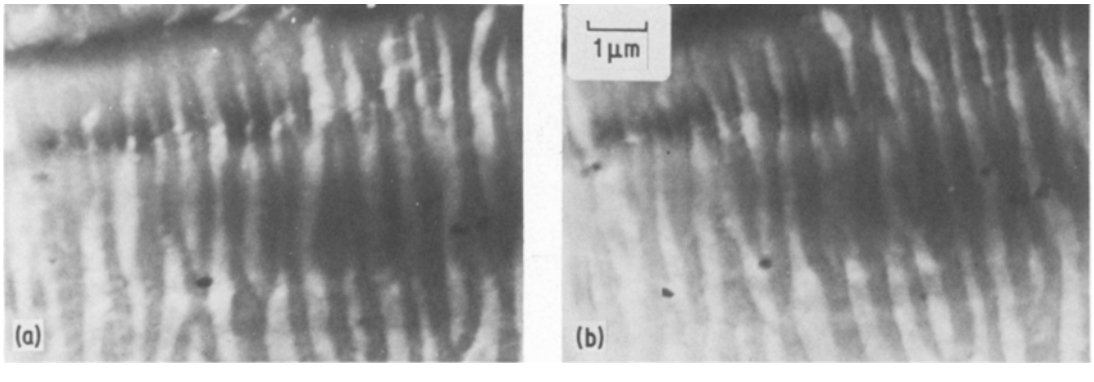

Figure 5 (a) Dark field image formed from one wing of the meridional reflected. (b) Corresponding dark field image formed in the other wing of the meridional reflection.

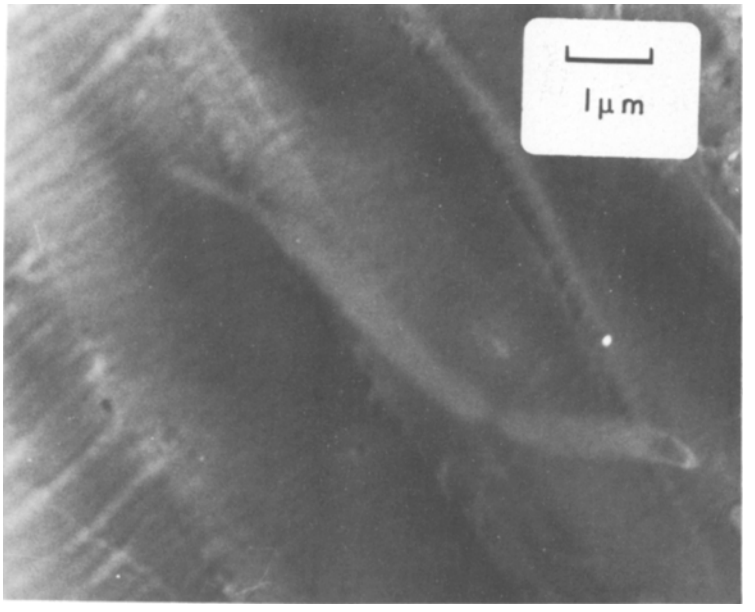

Figure 6 Low contrast dark field image formed from the centre of the meridional reflection.

limited, range of molecular orientation. Thus, although there is the advantage that dark field electron microscopy gives information about the actual molecular director, rather than just an optical director, it does not give the same level of resolution in orientation terms as does optical microscopy. Improved orientational resolution is obtainable by recourse to microdiffraction techniques, whereby diffraction patterns may be obtained from regions abot 0.3 μm in diameter (as limited by radiation damage of the polymer and not the probe size of the electon microscope). Such experiments are in progress.

However, the micrographs in this study do more than confirm that the banded structures are associated with a serpentine trajectory of the molecular axis about the shear direction: Figs. 3a and b show that the width of the diffracting regions increases as the position of the objective aperture is moved closer to the centre of the equatorial arc. This indicates that the molecular axis changes continuously with position in accord with the analysis of the optical director [1]. If only two discrete orientations were present, as is proposed for the pleated sheet structure of Kevlar [2], then the width of each band would not change in response to such a change in aperture postion, and indeed the equatorial reflection would be expected to split into discrete maxima above and below the equator.

The model thus proposed can also explain the observation demonstrated by Fig. 4b that the periodicity halves when the central portion of the equatorial reflection is used to form the dark field

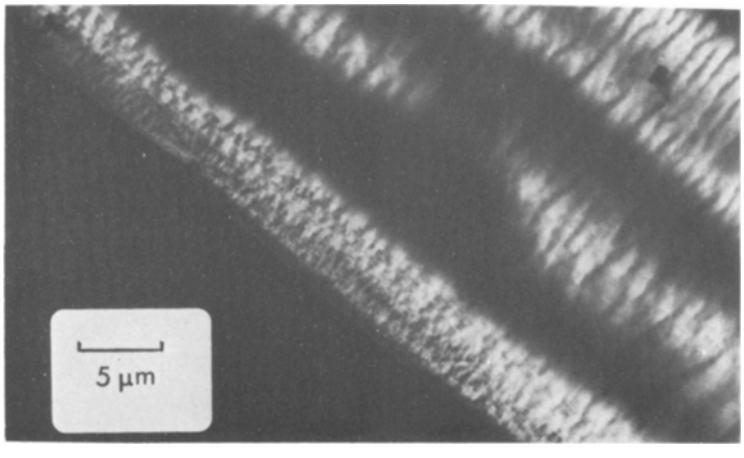

Figure 7 Periodicity change in the banded structure at the edge of a film of B–N.

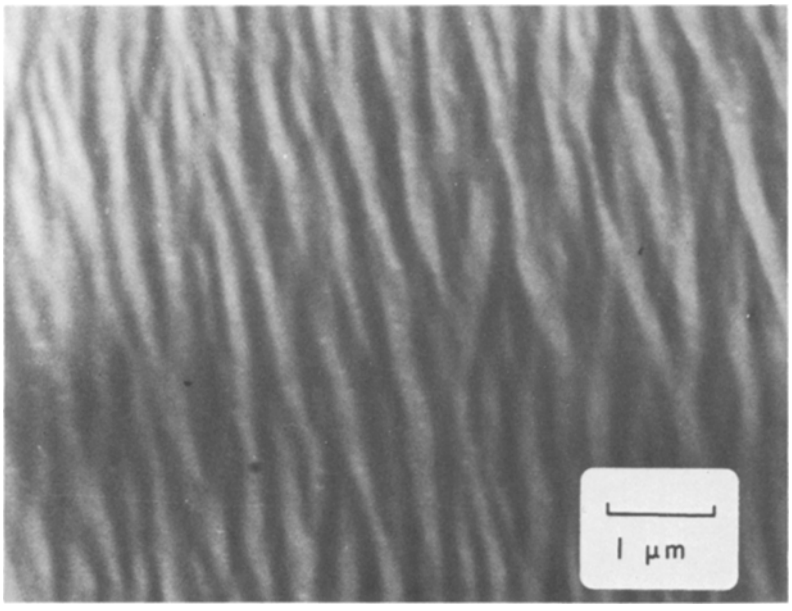

Figure 8 Banded structure in N–AT: dark field image formed in one wing of the equatorial reflection.

image. This result is equivalent to a halving in the periodicity observed optically when the analyser (or crossed polarizer) is precisely aligned with the shear direction [1], and the same explanation can be invoked; the two extremes of the chain axis orientations are equivalent in direction and thus will both contribute to the image. In the central part of the meridional, however, zero or low contrast is seen. For perfectly-oriented molecules the meridionals would be layer lines. The serpentine packing of molecules merely causes these to be smeared out into an arc, but for each locally aligned region, some part of its layer line will be accepted by the objective aperture resulting in effectively zero overall contrast.

Although the confirmation by electron microscopy of the simple serpentine packing model of banded microstructures appears clear cut, it is important that the equivalence of optical and molecular directors demonstrated in this case, is not taken to be generally true. Indeed, there seem to be some related areas in which particular caution is appropriate. Firstly, there is evidence that in specimens which are less well oriented than the sheared films used in this work the direct correlation between the optical textures (not banded) and the range of orientations indicated by either X-ray or electron diffraction can be completely lost. The resolution of this paradox may involve the possible rotational correlation of groups of molecules about their long axes. Secondly, detailed X-ray analysis of relatively poorly oriented specimens [7], shows that the orientation as determined from the azimuthal sharpness of the equatorial maxima is always greater than that indicated by the meridional reflections, which appear more "arced". Electron diffraction patterns show the same effect. It may thus be that the diffracting regions imaged in dark field may not be truly axially symmetric about the molecular long axes. Finally, it must be emphasized that the electron microscopy has been interpreted in terms of deviations of the molecular director in the plane of the specimen. That the optical director may not lie completely within this plane was suggested by the phase contrast work reported in the preceding paper [1]. However, while there is a probability that corresponding out of plane deviations of the molecular director may be present, they should have little effect on the dark field microstructure as imaged in the equatorial reflection.

Banded structures appear to be a general feature of liquid crystalline polymers oriented by flow; however, the reason for their formation is less forthcoming. In the course of the present work it has only been possible to examine the nature of the structure once it has formed and been quenched in. The only *in situ* experiments on any equivalent structures reported in the literature to date are those due to Kiss and Porter [8] on the synthetic polypeptide poly (γ-benzyl-L-glutamate) (PBLG). These observations indicate that the texture, termed by them the "row

nucleated" texture, only formed under specific conditions in terms of shear rate and concentration of the polymer in m-cresol (PBLG is lyotropic exhibiting cholesteric mesophases that may "unwind" during shear). Specifically, it was found that the banded structure formed at relatively high shear rates for the most concentrated solution, but for lower concentrations the texture formed only upon cessation of shear (i.e. as a relaxation phenomenon). During relaxation, the rate at which the striations appeared depended upon the prior rate of shear, being more rapid the higher the shear rate (and also subsequently degenerating faster); furthermore, periodicity of the structure decreased as shear rate increased. These observations are consistent with the effect shown in Fig. 7, where the period decreases at the thin edges where the shear rate is highest. Since any variation in specimen thickness will cause changes in the shear rate disturbances of the regularity of the banding are to be expected at these points, as is observed. The somewhat smaller periodicity seen in the TEM compared with the light microscope can be rationalized by the same argument, since only the thinnest regions can be studied in the TEM. It is perhaps also of significance that the TEM study on Kevlar [2] also noted a change in periodicity at the edges of the fibre, where spinning conditions will differ significantly from the central portion.

5. Conclusions

This TEM study complements the previous paper describing the optical properties of the banded structure [1]. From the analysis of the dark field images formed in equatorial and meridional reflections it is clear that the near-sinusoidal variation in the direction of the principal axis of the refractive index ellipsoid is indeed reflecting the variation in the molecular orientation. The TEM results also confirm that the transitions from one orientation to another are smooth rather than abrupt kinks even in the thinnest specimens.

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